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An advanced OMVPE process is being developed for the deposition of III-V semiconductor materials and structures. There are important optoelectronic device structures which can not be realized by conventional means. These include AlGaAs semiconductor lasers with improved coherence using embedded diffraction gratings, and GaInP pseudomorphic structures on GaP substrates for short wavelength semiconductor lasers. The structure on GaP result in improved laser performance compared to the 650 nm AlGaInP devices previously developed in this program. The new OMVPE apparatus combines the multichamber reaction cell with deep UV photo-assisted growth and modulation flow epitaxial techniques. Using a combination of such processes, the growth temperature requirements for III-V alloys can be substantially reduced. Selective growth on a sub-micron scale will be attempted with in-situ interference holography. The materials and techniques developed in this research program will result in significant simplifications to the fabrication sequence required to realize complex integrated optoelectronic circuits.

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I. Introduction

This program has endured a transition period while the construction of Cornell's new OMVPE laboratory is completed. A 18 month design phase came to completion in July, 1989 and construction is scheduled to be complete in April, 1990. This lab will allow a significant expansion of the OMVPE research facilitated by the existing machine, the SDIO machine, and the multichamber apparatus recently donated by General Electric. Over the last year, research activities have shifted to device fabrication and materials characterization studies, while the "new materials supply" has been interupted by the facility upgrade. The OMVPE reactor funded by this program has been assembled in modular fashion and will be operational soon after the opening of the new laboratory.

In the past year, many accomplishments which focus on quantum well laser devices have been realized. For example. progress has been made on incorporating disordered low loss regions in surface emitting laser arrays in collaboration with SRI-Sarnoff. Also, a new Raman microprobe has been used to observed the vibrational modes of a single quantum well at room temperature. This is the first report of the non-resonant observation of <u>single</u> quantum well heterostructures with Raman spectroscopy.

II. Progress in the Past Year

The progress in the last year of this program has been highlighted below and appears in 4 sections. First, the Cornell's new Compound Semiconductor Materials Laboratory has required an enormous design activity and a fund raising effort. This facility meets the most stringent fire and safety code structure found in the US. A brief description of its capabilities and its purpose are outlined. Next, the status of the SDIO OMVPE reactor will be reviewed. Finally, 2 key research activities which focus on quantum well laser characterization and development will be discussed.

<u>L</u>angmuir <u>C</u>ompound <u>S</u>emiconductor <u>M</u>aterials <u>L</u>aboratory (LCSM)

The LCSM laboratory is a 3 OMVPE reactor and device processing facility for III-V semiconductor materials and optoelectronic devices. The lab required roughly a $ 3M investment to upgrade Cornell's semiconductor materials research programs. This new facility complements the advanced fabrication technology available at Cornell through the <u>N</u>ational <u>N</u>anofabrication <u>F</u>acility (NNF). The university, several industries, and US Government programs like this SDIO/IST contract, have shared in providing the support required. For this program, the contribution to the facility is the funding of the 3rd generation OMVPE reactor.

The lab's floor plan is shown in figure 1. The 3 OMVPE reactors are shown along with their sponser indicated in parenthesis. A separate materials storage room which houses the arsine and phosphine and other reactants such as dopant gas mixtures is only accessable from outside as shown. A vented raceway surrounds the toxic gas supply piping which delivers the gas to each reactor. The facility has a total of 5000 sq. ft. of floor space with 2000 sq. ft. of class 10,000 laminar flow clean space. The exhaust gases are incinerated with a newly developed (and partially donated) system

from Heat Ultrasonics. This new incineration technology makes it possible to treat high concentrations of toxic gas which appears at its inlet. As a result. a secondary enclosure system for arsine and phosphine can be implimented to contain a release from catostrophic cylinder failure. This is the only facility in the US which can support such a claim. Many design and implimentation aspects of this laboratory can and should serve as a model for new US government and industry OMVPE laboratory installations.
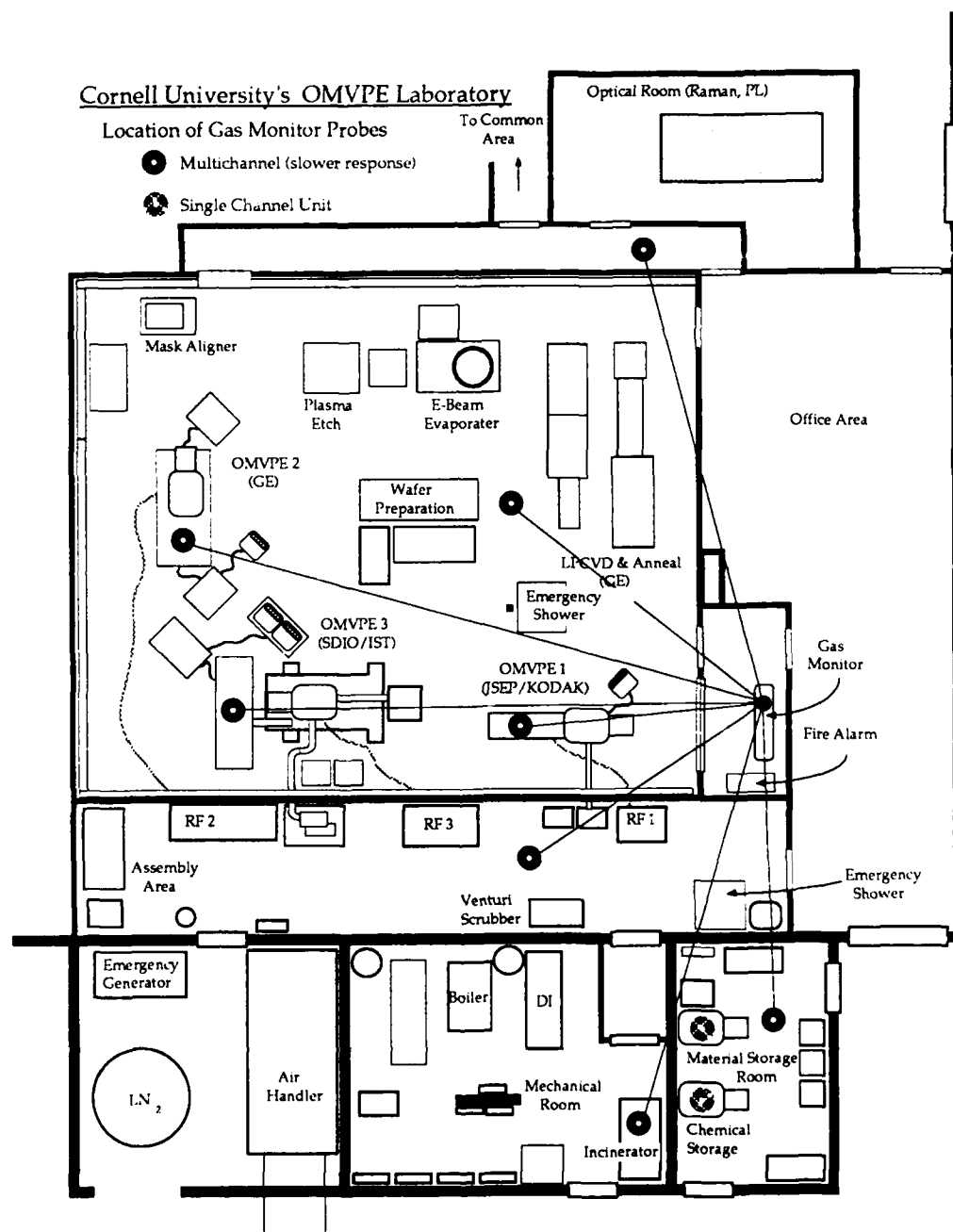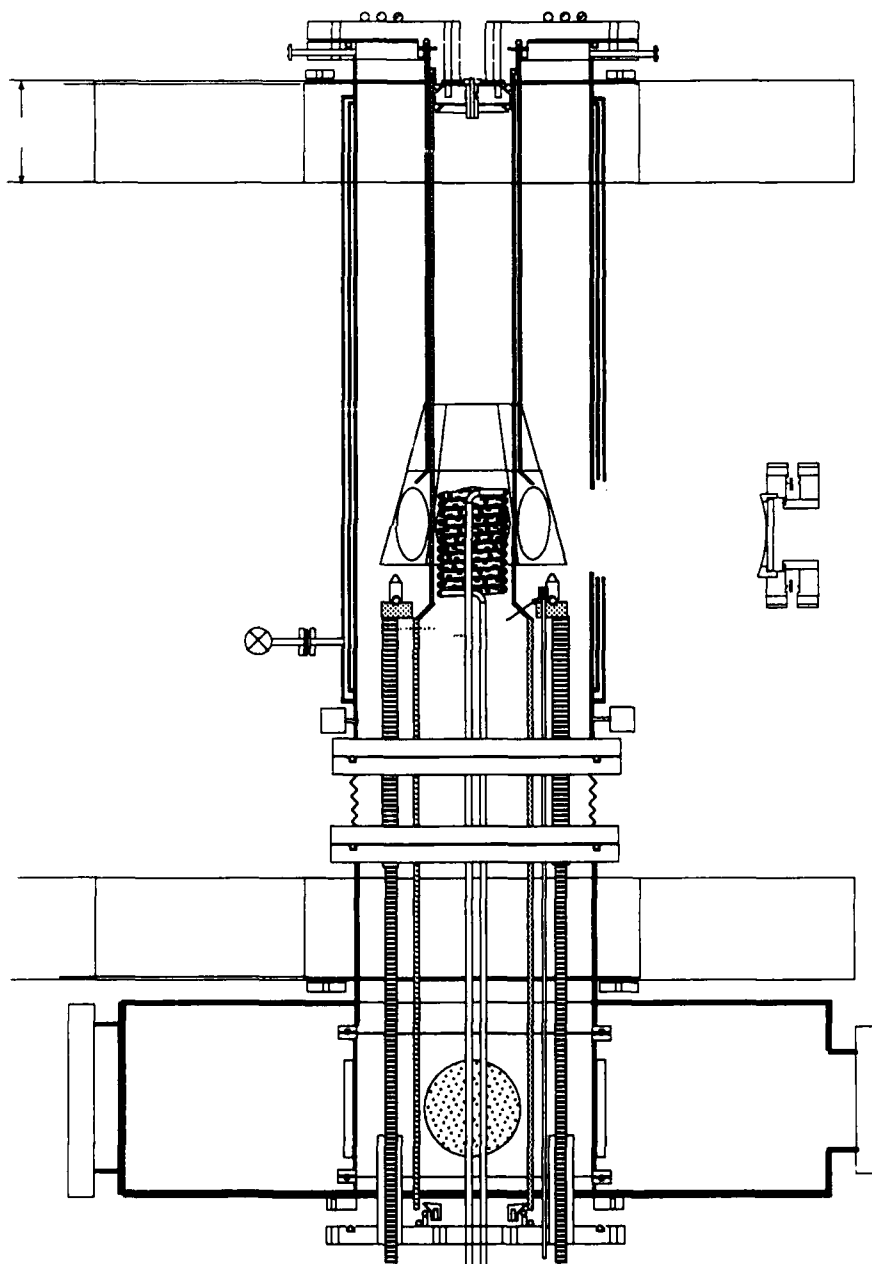
Cornell University's OMVPE Laboratory

Location of Gas Monitor Probes

● Multichannel (slower response)

◉ Single Channel Unit

Optical Room (Raman, PL)

To Common Area

Mask Aligner

Plasma Etch

E-Beam Evaporater

Office Area

OMVPE 2 (GE)

Wafer Preparation

LPCVD & Anneal (GE)

Emergency Shower

OMVPE 3 (SDIO/IST)

OMVPE 1 (JSEP/KODAK)

Gas Monitor

Fire Alarm

RF 2

RF 3

RF 1

Assembly Area

Emergency Shower

Venturi Scrubber

Emergency Generator

Boiler

DI

Material Storage Room

Air Handler

LN$_2$

Mechanical Room

Chemical Storage

Incinerator

Figure 1. Floor plan of the LCSM. The facility is placed in a recently constructed building located in Cornell's Research Park located near the Ithaca airport.

Reactor Design & Construction

The SDIO reactor under construction in this program is broken up into several modules which provide for the key features of this apparatus. These modules are the gas handling and distribution system. the UHV system used for in-situ mass analysis, the high throughput low vacuum pumping system, the in-situ Raman system, and finally, the reaction cell/optical bench support structure. With the exception of a few components of the reaction cell, all construction on this machine is complete and awaits the installation in the laboratory. The design of the reaction cell is presented below in figure 2.

Figure 2. Schematic representation of the SDIO OMVPE reaction cell. The cell is a vertical barrel design with a cooled stainless steel reactor wall.

This cell will accomodate 4 separate deposition zones, one of which is accessed by a UV transparent optical window for selective growth studies and in-situ Raman. The support structure is a 3 platform optical table which was custom built by Newport Research. Shown at the lower portion of figure 2, the cell has a large throughput particulate filter which avoids degradation of the downstream vaccum system components. With the multichamber design used here, this system will be particularly suitable for ALE or flow modulation growth studies.

Optoelectronic Device Fabrication

The use of selective heterostructure disordering has profound impact on the fabrication of complex optoelectronic integrated circuits. The ability to intermix quantum well heterostructures opens the possibility to the fabrication and integration of novel optical devices since it allows the post growth alteration of the effective bandgap. Several III-V semiconductor material types have been selectively intermixed by using a method which is less complicated than many other methods. The method involves the rapid thermal annealing of SiO_2 encapsulated samples. Selective intermixing has been observed for four material types: GaAs/AlGaAs on GaAs, GaInAs/AlGaAs on GaAs (pseudomorphic structures), GaInAs/AlInAs on InP and GaInP/AlInP on GaAs. The degree of intermixing has been characterized by photoluminescence (PL), Raman and photocurrent spectroscopies. The intermixing mechanisms for each of these material types has also been investigated by using Secondary Ion Mass Spectroscopy (SIMS) and Auger spectroscopy. The intermixing process for each of these material types is summarized in table 1 which shows the wavelength range, the observed shifting of the bandgap, the range of annealing temperature and time, the effects on the PL efficiency and the intermixing mechanism.

The peak PL energy can be shifted by several hundred angstroms while still maintaining approximately the same linewidth. The PL effeciencies can be altered significantly during the annealing process. For the GaAs/AlGaAs and the GaInAs/AlGaAs materials grown on GaAs the PL efficiencies are typically reduced by a factor of 2 to 4 for shifts of 100-200 Å. It may be possible to recover some of this loss by subsequent low temperature anneals. For the other two materials significant increases in the PL efficiencies were observed after the intermixing/annealing process. This is most likely due the existence of a large number of non-radiative defects in these types of material. For the GaInAs/AlInAs quantum well structures grown on InP 15-fold increases were observed and showed clear trends with well width. This, in and of itself should prove valuable in the fabrication of optical devices in the 1.1-1.6 μ range. SIMS and Auger depth profiling varified that the intermixing mechanisms were either an impurity-free Ga vacancy related process or an impurity-induced (Si) related process. For the higher quality material there was no Si incorporation into the heterostructures while there was Ga deficient regions near the surface, which shows that the intermixing is caused by Ga out-diffusion into the SiO2. For the lower quality material, however, there was significant Si incorporation into the samples. For example, for the GaInAs/AlInAs quantum wells the Si diffused approximately 0.5 μ into the samples in only 15 seconds. The existing defects in the as-grown crystal could clearly be the catylist for the Si diffusion.

Table 1. Summary of results of intermixing experiments of the III-V materials systems under investigation.

Material	Nominal Wavelength	Wavelength Shift	Temperature	Time	PL Efficiency	Intermixing Mechanism
GaInAs/AlInAs on InP	1.3 μ	0 - 700 Å	750-900°C	15 s	5 to 15 fold increases	Impurity Induced $\left\{ [Si] > 10^{18} cm^{-3} \right\}$
GaInAs/AlGaAs on GaAs	0.9 μ	0 - 150 Å	850-950°C	15-30 s	not measured	Ga Vacancy
GaAs/AlGaAs on GaAs	0.84 μ	0 - 500 Å	850-975°C	15 s	0 to 5 fold decreases	Ga Vacancy
GaInP/AlInP on GaAs	0.65 μ	0 - 200 Å	800-975°C	15 s	0 to 4 fold increases	Impurity Induced and/or Ga Vacancy $\left\{ [Si] = 10^{18} cm^{-3} \right\}$

In a collaborative effort with SRI-Sarnoff Laboratories, the fabrication of surface emitting lasers which use the selective intermixing process to make the grating regions *transparent are presently being pursued.*The differential loss in the grating sections should be approximately 50 cm^{-1} which translates to approximately a factor of four for a 300 μ grating section. This improvement will imply significantly lower threshold currents, higher efficiencies and larger obtainable optical powers. The use of the intermixing process to fabricate planar index guided gain sections instead of etched ridge gain sections is also being investigated.

Figure 3. Diagram of the optoelectronic integrated circuit currently being fabricated with the selective intermixing process.

The intermixing process also provides a means to integrate optical devices. The fabrication of a circuit which will integrate a laser, a transparent waveguide and an

modulator is currently underway. A schematic diagram of the structure is shown in figure 3. It shows the laser surrounded by feedback gratings followed by a 1 mm waveguide section and a 250 μ modulator section. The modulator will be "tuned" to the laser by selecting the appropriate grating period. The modulator will operate via the Stark effect which is the shifting of the effective bandgap due to an applied voltage.

Materials Characterization

Raman spectroscopy has been used to study graded index-separate confinement heterostructure (GRIN-SCH) semiconductor lasers. In these experiments, a forward scattering geometry in which the laser is endfired, and the light emerging from the opposite end facet is collected and spectrally analyzed. In this configuration the waveguide confines the Raman probe, and thus interacts with the entire laser cavity. This permits nonresonant observation at room temperature of the vibrations in a single 100 Åquantum well active region. The results show that Raman scattering is a useful measure of the mode profile in waveguide heterostructures. We have also observed inhomogeneously broadened LO and TO phonons in the graded region.
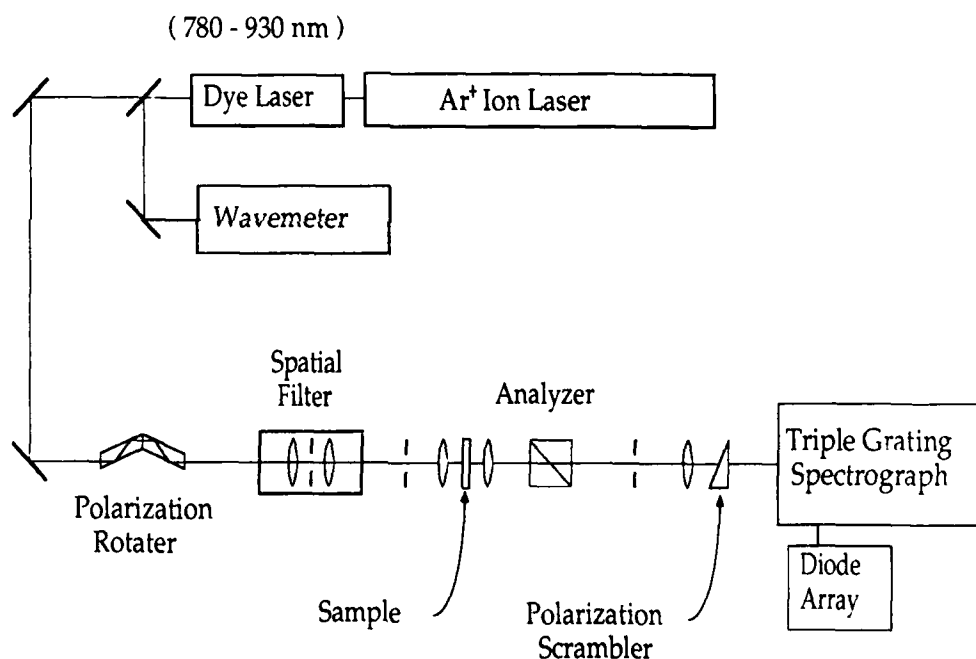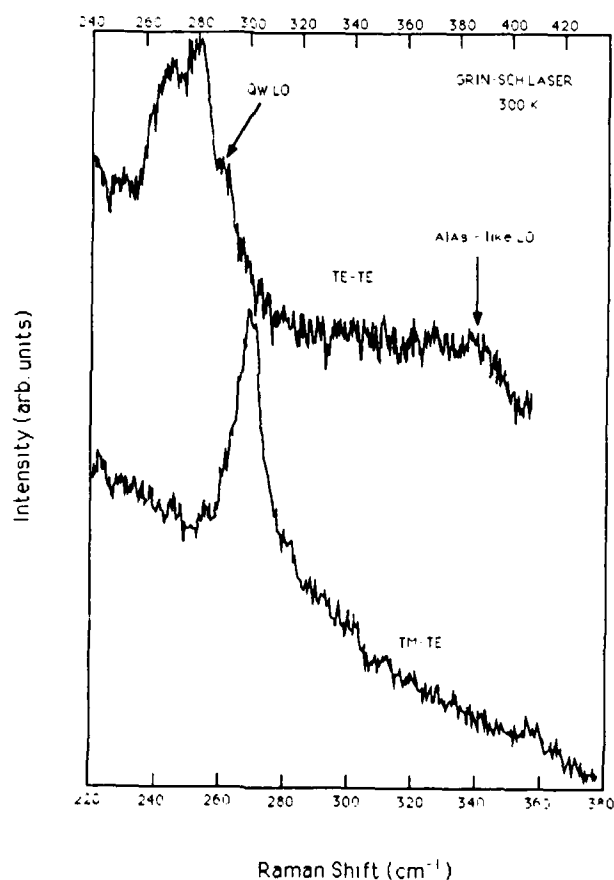
Figure 4. Schematic illustration of the Raman apparatus used for the GRIN-SCH laser studies.

Figure 4 shows a diagram of the experimental apparatus. The output beam of an Ar+ pumped Styryl 9M cw dye laser (780 - 930 nm) was focussed with a 0.50 N.A. (numerical aperature) microscope objective to an approximately 1.8 μ diameter spot on a (110) cleavage plane of the device. A commercial interferometer (Burleigh Instruments) was used to measure the wavelength of the dye laser. After passing through a broadband (700-1000 nm) polarization rotator, the incident beam was spatially filtered with a combination of two 0.25 N.A. microscope objectives and a 25 μ pinhole. The sample was mounted on a three axis rotation stage which permitted precise alignment

of the sample facet normal to the incident beam. This provided optimal coupling of the input laser beam to the waveguide modes. The alignment was checked by observing the back reflection from the facet on an iris diaphragm. A 0.6 N.A. objective was used to image the near field radiation pattern on a slit which blocked any stray unguided light collected by the objective at the exit facet. This stray light was usually quite weak. The desired polarization of the scattered light was selected with a polarizing beamsplitter. Finally, the light passed through a focussing lens and polarization scrambler before entering a triple grating spectrograph. The scattered light was detected with a 1024 element diode array controlled by an optical multichannel analyzer. The power of the dye laser beam was approximately 35 mw at 905 nm. This wavelength was selected to be well below the fundamental absorption edge of the active region. All spectra were taken in the forward scattering geometry at 300 K.

Figure 5. Raman spectrum of a GRIN-SCH single quantum well laser structure taken at 300 K. This data represents the first non-resonant Raman observation of the vibrational modes of a single quantum well.

Figure 5 shows spectra of a standard single quantum well GRIN-SCH laser taken in two different polarization configurations. In the waveguide, the boundary conditions imply that light scattering occurs between laterally confined wave-packet states, unlike scattering between plane waves in bulk. It is apparent that the spectrum is strongly

dependent on the polarization of the incident and scattered guided modes. When both modes are TE polarized, longitudinal and transverse phonons are seen, whereas if the incident and scattered modes are cross polarized, only vibrations at the transverse frequency appear. We observed no scattering in the TM-TM configuration. GaAs-like and AlAs-like longitudinal vibrations and the GaAs-like TO phonon of the graded index region are evident as well as the LO phonon of the quantum well. The latter is a shoulder on the high energy side of the GaAs-like LO. The TO phonon in the quantum well cannot be resolved from the inhomogeneously broadened GaAs-like TO feature of the GRIN layer. Small displacements of the input dye laser beam at the end facet of the sample caused the relative strength of the quantum well and GRIN features to vary, indicating the sensitivity of the spectrum to the incident guided mode. In this context, Raman spectroscopy is a useful indication of guided mode profile because the signal strength of a particular excitation is proportional to the intensity of the optical mode in the corresponding region of the heterostructure. The GaAs-like LO and TO features of the graded index region occur at 279 and 269 wavenumbers, respectively. This corresponds to 30 % AlGaAs; however, the HWHM of the LO feature is considerably broader than the linewidths previously reported for this material because of the wide composition grading. The LO peak of the quantum well appears at 289 wavenumbers, indicating alloying on the order of 10 %.

The immediate applications of this work include characterization of single pseudomorphic thin films, which are currently of great interest for electronic and optical applications, and the study of fundamental processes in semiconductor lasers. Recently there has been some indication that photoexcited LO phonons may participate in stimulated emission in $GaAs/Al_xGa_{1-x}As$ quantum well heterostructures. Such nonequilibrium phonon distributions should be readily observable with Raman spectroscopy. Study of electron-phonon coupling and the single particle and collective excitations of the degenerate Fermi gas of electrons and holes in a forward biased device could yield much information about many body processes in semiconductor lasers.

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Summary

The SDIO program has strengthened the III-V semiconductor materials related activies at Cornell. Sucessfull transistion of this technology to US industy has occcured over the last year. The selective disordering process has been implemented in an improved 2D surface emitting laser array at SRI-Sarnoff. The visible AlGaInP device technology has been used in a prototype plastic optical fiber communication system for local area networks by Codenoll Corp. Our cost sharing and collaboration with SRI-Sarnoff has resulted in an increased emphasis on exploiting Cornell's semiconductor materials technology in new optoelectronic devices. In addition, progress in the last year has included the refinement of Raman scattering in the waveguide geometry, which has produced significant signal from the single quantum well active region in a high performance GRIN-SCH laser. This technique offers an important diagnostic tool (passive probe) which can be used on lasers during operation. Finally, this program can look foward to the increased OMVPE crystal growth activity at Cornell when 3 reactors are commissioned in the new facility in 1990.